
Heavy metal contents in the most productive Argentinean Humid Pampa soils

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Abstract: Argentinean Humid Pampa topsoil samples from sites with different land use patterns were analysed. Texture was dominated by fines (silt+clay > 50%) with high total organic carbon content ($2.8 \pm 1.8\%$), particularly in finer soils (3.7–9.9% to 0.99% in sandy soils). Carbon:nitrogen relationship was relatively homogeneous ($13.9 \pm 3.6\%$) pointing to a dominant contribution of terrestrial plant detritus. Heavy metal concentrations were low (Fe: $1.77 \pm 0.50\%$; Mn: 446 ± 171 ; Zn: 48.4 ± 19.5 ; Cu: 17.6 ± 6.0 ; Pb: 10.0 ± 4.8 ; Cr: 7.2 ± 1.8 ; Ni: 6.1 ± 1.7 ; Cd: $0.05 \pm 0.03 \mu\text{g g}^{-1}$) and spatially homogeneous (<50%) with more variability for Cd ($\pm 58\%$); the exception was an industrial site with atypically high values for Zn ($111 \mu\text{g g}^{-1}$) and Cr ($11.9 \mu\text{g g}^{-1}$). Heavy metal levels were lower than the Soil Environmental Quality Guidelines for Agriculture land use established in international legislation. Mn-Cu-Pb-Ni-Cd-Cr exhibited positive correlations with soil fine contents ($R^2_{\text{Mn}} = 0.76$; $R^2_{\text{Cu}} = 0.73$; $R^2_{\text{Pb}} = 0.73$; $R^2_{\text{Ni}} = 0.56$; $R^2_{\text{Cd}} = 0.45$; $R^2_{\text{Cr}} = 0.38$; $p > 0.05$). Heavy metal enrichment factors were low (0.07–2.28) indicating a natural origin.

Keywords: soil; heavy metals; C:N relationship; texture composition; Argentinean Humid Pampa.

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1 Introduction

Heavy metals are one of the groups of soil contaminants of major concern due to the marked increased in their production and release into the environment in the last decades (Nriagu and Pacyna, 1988; Nriagu, 1990; Adriano, 2001; Han et al., 2002; Kabata-Pendias and Mukherjee, 2007; Alloway, 2013). Some of them, so called micronutrients, like Fe, Mn, Zn, Cu and Cr are essential for life but in high concentrations have adverse effects; on the other hand, Cd, Ni and Pb are highly toxic (Wood, 1974; Nordberg et al., 2002; Liu et al., 2008).

The principal sources of heavy metals in soils include geological parent materials and anthropogenic inputs derived from agriculture practices (fertiliser and pesticide application), the disposal of municipal wastes and sewage sludge, a wide variety of industrial and mining operations, and traffic-related activities that increase natural burdens directly on soil surface or via the atmosphere as dry and wet deposition (Senesi

and Polemio, 1981; Ure and Berrow, 1982; Bilos et al., 2001; Amusan et al., 2003; Cheng, 2003; Nicholson et al., 2003; Conko et al., 2004; He et al., 2005; Rossini Oliva and Fernández Espinosa, 2007; Bermúdez et al., 2010). Soils also act as sources of heavy metals to the atmosphere, via resuspension of dust particles, or to surrounding aquatic ecosystems through water runoff transport, dissolved or associated to particles (Nriagu, 1979, 1989; Mason et al., 1999; Wong et al., 2006; Pereira et al., 2007; Murakami et al., 2008; Kabata-Pendias, 2011).

Soil texture composition, pH and the presence of other factors in soil solution (complexing ligands, ionic strength and competing metals) significantly affect heavy metals sorption processes and leaching potential through the soil profile (Tack and Verloo, 1995; Ashworth and Alloway, 2008; Zubillaga et al., 2008; Zubillaga and Lavado, 2008; Kabata-Pendias, 2011). The mobile forms of these elements constitute a risk as they may reach groundwater and be consumed by humans (Oliver, 1997; Harter and Naidu, 2001; Ammann et al., 2003; Heredia and Fernández Cirelli, 2009). Another important route for human intake of heavy metals are crops, particularly accumulating species from natural rich or polluted soils, and grazing livestock (Dudka and Miller, 1999; Kabata-Pendias, 2004; Lavado, 2006; Lavado et al., 2007; Bermúdez et al., 2011; Salazar et al., 2012).

In this paper we evaluate the biogeochemistry of heavy metals in Humid Pampa soils affected by different land uses in Buenos Aires Province to determine the concentration patterns related to the grain size composition and total organic carbon contents of soils and the impact of human activities.

2 Materials and methods

2.1 Study area

The Argentinean Pampa covers the extensive plains of the Provinces of Buenos Aires, La Pampa, Córdoba, Santa Fe, San Luis and the east of Entre Ríos. The Buenos Aires Province in particular, mainly located in the Humid Pampa, is predominantly flat and covered by soils of the Mollisols order developed from loess deposits of Pleistocene age. These aeolian sediments have physical characteristics that favour the formation of well structured soils with deep, dark-coloured horizons, appropriate for root development (Teruggi, 1957; Soil Survey Staff, 1975; Taylor et al., 1983; Alvarez and Lavado, 1998; Moscatelli and Pazos, 2000).

This region is one of the largest temperate areas of the Southern Hemisphere used for agriculture and intensive cattle production. Manufacturing industries are mainly located in the outskirts of some important cities, and mining activities are not relevant and limited to certain areas. The climate of the region is temperate with mean annual temperature ranging from 15°C to 20°C (south to north), and average rainfall from 600 mm to 1000 mm (southwest to northeast; Grossi Gallego and Lopardo, 1988). Its native vegetation consists of grasslands dominated by perennial graminaceous species (e.g.: *Piptochaetium* spp.; *Poa* spp.; *Stipa* spp.).

2.2 Sampling

Composite topsoil samples (0–10 cm depth; $n = 22$) were taken from 15 sampling sites with different land use, covering a surface area of about 307,500 km² in the Buenos Aires Province (Figure 1; Table 1). Samples were collected with a stainless steel hand-spade aggregating 5–6 increments from each sampling point, taking care of removing the surface grass layer and coarse debris. Samples were stored in prewashed (HNO₃ 10% solution, 24 h) glass containers (500 mL) and transported refrigerated to the laboratory.

Figure 1 Study area and location of sampling sites

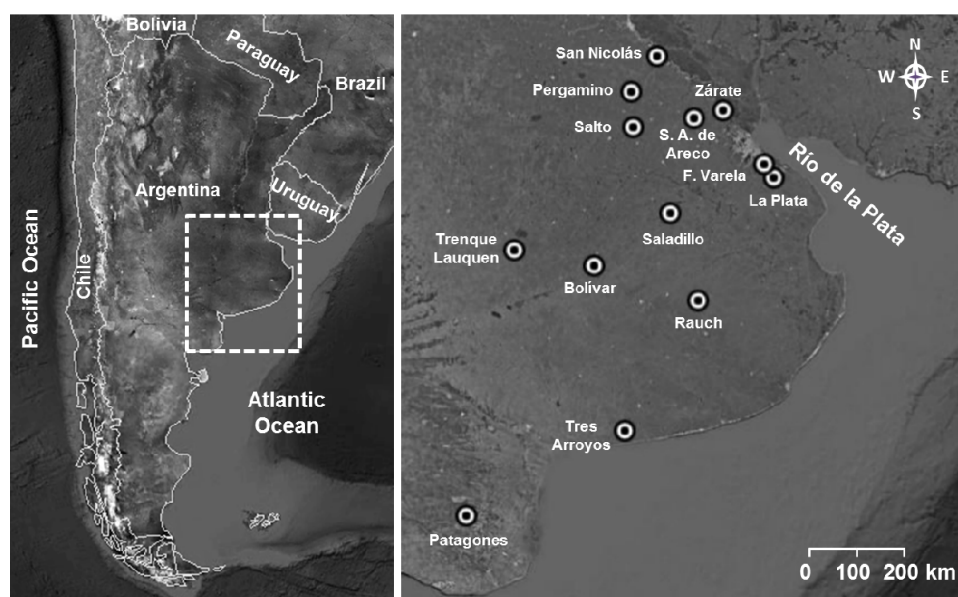


Table 1 Sampling site location and land use pattern

Sampling site	Location	Textural class	Classification	Land use
San Nicolás	S 33° 22' 29.13" W 60° 10' 19.00"	Silty clay loam	Mollisol Vertic Argiudoll	Recreational activities. Suburban grassland, nearby a metallurgy industrial area
Pergamino	S 33° 54' 04.31" W 60° 35' 33.26"	Silt loam	Mollisol Typic Argiudoll	Recreational activities. Suburban grassland
Zárte	S 34° 06' 22.22" W 59° 00' 02.68"	Clay loam	Mollisol Vertic Argiudoll	Recreational activities. Suburban grassland
San Antonio de Areco	S 34° 14' 25.42" W 59° 29' 45.35"	Silt loam	Mollisol Petrocalcic Paleudoll	Farmland, natural grassland
Salto	S 34° 24' 24.30" W 60° 32' 17.99"	Silt loam	Mollisol Typic Argiudoll	Farmland, soybean crop

Table 1 Sampling site location and land use pattern (continued)

<i>Sampling site</i>	<i>Location</i>	<i>Textural class</i>	<i>Classification</i>	<i>Land use</i>
Florencio Varela 1A	S 34° 50' 24.60" W 58° 14' 31.10"	Silty clay loam	Mollisol Abruptic Argiudoll	Farmland, floriculture production. Buenos Aires City horticultural belt
Florencio Varela 1B		Silty clay loam		Greenhouse, floriculture production. Buenos Aires City horticultural belt
Florencio Varela 2		Silt loam		Natural grassland. Buenos Aires City horticultural belt
La Plata 1A	S 35° 01' 27.90"	Silty clay loam	Mollisol	Farmland, organic horticulture production. La Plata City horticultural belt
La Plata 1B	W 58° 03' 36.20"	Silty clay loam	Aquic Paleudoll	
La Plata 2A	S 35° 01' 04.00"	Silty clay loam	Mollisol	Farmland, traditional horticulture production. La Plata City horticultural belt
La Plata 2B	W 58° 02' 10.10"	Silty clay loam	Aquic Paleudoll	
La Plata 2C		Silty clay loam		Greenhouse. La Plata City horticultural belt
Saladillo 1	S 35° 36' 30.50" W 59° 50' 14.00"	Sandy loam	Mollisol Typic Natraquoll	Farmland, corn crop
Saladillo 2	S 35° 37' 16.40" W 59° 47' 44.20"	Sandy loam	Mollisol Thaptoargilic Hapludoll	Farmland, organic seeded pasture for intensive livestock production
Trenque Lauquen 1	S 36° 11' 56.90" W 62° 33' 07.70"	Loam	Mollisol	Farmland, corn crop
Trenque Lauquen 2		Loam	Entic Hapludoll	Farmland, soybean crop
Bolívar 1	S 36° 23' 38.20"	Sand	Mollisol	Farmland, soybean crop
Bolívar 2	W 61° 08' 30.30"	Loamy sand	Entic Hapludoll	Farmland, feedlot livestock production
Rauch	S 36° 49' 51.80" W 59° 16' 43.00"	Silt loam	Mollisol Typic Argiudoll	Farmland, seeded pasture for intensive livestock production
Tres Arroyos	S 38° 43' 31.70" W 60° 29' 33.20"	Silt loam	Mollisol Petrocalcic Argiudoll	Farmland, wheat and sunflower crops
Patagones	S 39° 59' 42.90" W 63° 22' 54.70"	Sandy loam	Aridisol Typic Haplocalcid	Farmland, natural grassland for extensive livestock production

2.3 Chemical analyses

Soil samples were homogenised and sub-sampled to determine gravimetrically water content (105°C, 24 h) and grain size composition (wet sieving and pipette method; Folk, 1980). The remaining sample was oven dried (35°C), crushed in a glass mortar and stored at room temperature until analysis.

Total organic carbon (TOC) and total nitrogen (TN) contents were determined by high temperature catalytic combustion with a Thermo Finnigan CE Flash EA 1112 elemental analyser. To eliminate inorganic carbon soil samples were treated with HCl 6N. The accuracy of TOC and TN determinations, evaluated through the analysis of certified reference materials including a high organic content sediment (B2150 Elemental MicroAnalysis Ltd.; %C = 6.10 and %N = 0.46) and a low organic content soil (B2152 Elemental MicroAnalysis Ltd.; %C = 1.52 and %N = 0.13), ranged from 85% to 115%.

For heavy metal analysis, soil samples were digested with aqua regia (3:1 v/v HCl to HNO₃) and H₂O₂ at 100°C (Hseu et al., 2002), the extracts were centrifuged, diluted to 25 mL with deionised water and stored in polyethylene bottles. Concentrations were determined using a Thermo Elemental Solaar M5 atomic absorption spectrophotometer equipped with a deuterium background corrector. Fe, Mn, Zn, Cu, Cr and Ni were measured in an air-acetylene flame while Cd concentrations were measured by using a GF95 graphite furnace with autosampler.

The quality assurance/control protocol included the analysis of procedural blanks (negligible), replicate samples ($n = 5$) to evaluate method precision (RSD < 10%) and triplicate analysis of Certified Reference Soil (CRM020-050, Resource Technology Corporation) to estimate method accuracy. The average recoveries ranged from 72% to 110% (Fe = $106 \pm 14\%$; Mn = $97.3 \pm 5.3\%$; Zn = $110 \pm 5.9\%$; Cu = $99.7 \pm 2.8\%$; Pb = $109 \pm 3.4\%$; Cr = $104 \pm 12\%$; Ni = $72.4 \pm 6.6\%$; and Cd = $87.3 \pm 2.2\%$).

2.4 Statistical analyses

The statistical work was performed with XLstat software (Addinsoft SRL, Paris) and included descriptive statistics, correlation and regression analyses. Normality of heavy metal data was evaluated with the Shapiro-Wilks test; in the case of Zn and Pb a natural logarithm (Ln) transformation was applied. The one-sided Grubbs test was applied to identify the presence of atypical values. Bonferroni's correction was applied to evaluate the significance in pairwise comparisons (corrected significance level $\alpha' = 0.002$) in multiple Pearson's correlation analyses. Exponential regression analyses were performed to evaluate the relationship of soils heavy metal concentration and fine grain contents. The significance level considered for all analyses was $\alpha = 0.05$.

3 Results and discussion

3.1 Grain size composition, TOC, TN and stoichiometric ratios

Soil texture was generally dominated by fine grain material, with clay (<0.002 mm) and silt (0.002–0.050 mm) representing more than 50% (Figure 2, Table 2). The sand fraction (0.050–2.00 mm) predominated (>60%) in three sampling sites located in the centre and the southwest of Buenos Aires Province (Bolívar, Saladillo and Patagones; Figure 1).

TOC contents ranged from ~1.0% in Patagones to 9.9% in San Nicolás with a relatively high average ($2.8 \pm 1.8\%$; Figure 2, Table 2). There was not a significant statistical correlation ($\alpha > 0.05$) between TOC and soil texture but finer silty clay loam and silt loam textural classes normally exhibited higher TOC values (Figure 3). These TOC contents were higher than those previously reported for the region (10–99 vs. 5.0–39 g TOC kg⁻¹; Alvarez and Lavado, 1998; Lavado et al., 1999; Lavado, 2006)

but in the same range than soils from Australia (11–31 g TOC kg⁻¹; Kirkby et al., 2011), China (3.2–83 g TOC kg⁻¹; Wang and Chen, 1998; Niu et al., 2013), Netherlands (21–78 g TOC kg⁻¹; Mulder and Elser, 2009), Poland (6.0–100 g TOC kg⁻¹; Dudka, 1992), Serbia (13–107 g TOC kg⁻¹; Dragović et al., 2008) or Spain (8.0–122 g TOC kg⁻¹; Tume et al., 2006).

Table 2 Fine grain size, TOC and TN contents, C:N stoichiometric ratios and heavy metal concentrations in soil samples

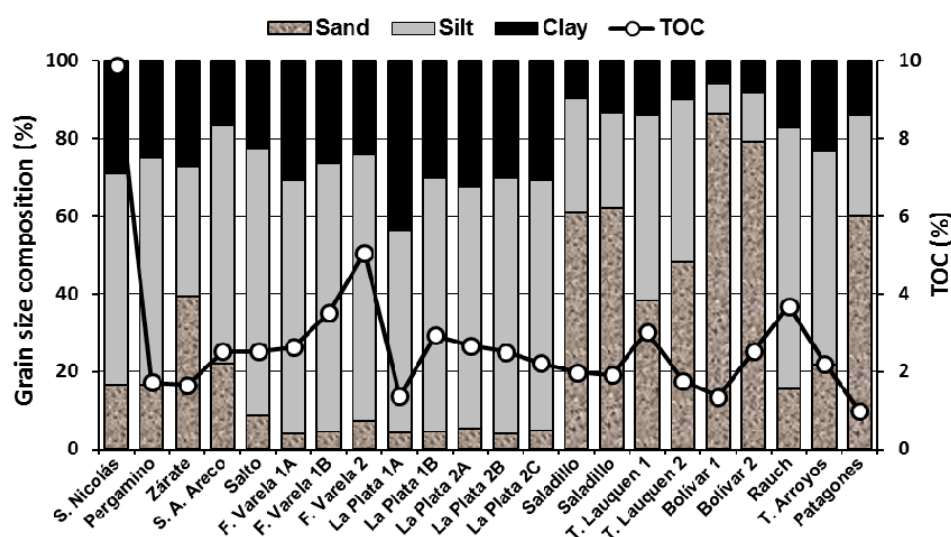
	Clay+Silt	TOC	TN		Fe	Mn	Zn	Cu	Pb	Cr	Ni	Cd
	%			C:N	%							
San Nicolás	83.4	9.88	0.57	20.1	2.63	580	111	22.2	18.2	11.9	9.4	0.03
Pergamino	83.4	1.73	0.13	15.3	2.31	477	71.7	20.3	15.7	8.8	7.9	0.10
Zárate	60.6	1.66	0.13	14.7	1.01	222	30.6	9.7	5.6	8.0	6.5	0.02
San Antonio de Areco	78.0	2.53	0.21	14.3	1.76	385	41.3	15.7	8.4	7.7	7.0	0.05
Salto	91.4	2.52	0.23	12.9	1.96	645	47.1	17.2	8.8	8.5	7.0	0.08
Florencio Varela 1A	96.2	2.63	0.36	8.6	1.52	595	86.5	23.3	17.5	8.1	6.9	0.11
Florencio Varela 1B	95.7	3.52	0.46	8.9	1.69	747	61.8	32.6	13.5	7.8	6.9	0.05
Florencio Varela 2	92.8	5.06	0.46	12.8	1.61	697	51.4	20.6	19.2	6.6	6.8	0.05
La Plata 1A	95.9	1.37	0.12	13.3	2.69	524	53.4	23.1	11.2	8.9	8.3	0.05
La Plata 1B	95.6	2.93	0.26	13.0	1.70	654	48.5	26.1	11.8	7.3	6.4	0.06
La Plata 2A	94.7	2.67	0.23	13.4	1.46	556	34.8	21.4	13.6	6.0	5.7	0.05
La Plata 2B	96.0	2.51	0.22	13.4	1.35	479	37.6	16.1	12.4	5.7	5.6	0.04
La Plata 2C	95.4	2.22	0.16	16.2	1.39	499	45.1	18.7	12.6	6.1	5.6	0.04
Saladillo 1	39.1	1.99	0.21	11.0	1.41	270	34.8	10.9	5.7	5.6	3.7	0.02
Saladillo 2	37.9	1.92	0.15	14.6	1.15	239	26.8	10.2	5.5	4.6	3.2	0.02
Trenque Lauquen 1	61.8	3.03	0.21	16.6	1.88	315	39.6	14.0	6.2	6.7	5.0	0.03
Trenque Lauquen 2	51.8	1.76	0.27	7.6	1.88	297	36.6	12.9	5.5	6.8	5.2	0.04
Bolívar 1	13.7	1.36	0.10	15.2	1.34	194	33.4	9.5	3.9	4.3	2.9	0.03
Bolívar 2	20.9	2.53	0.12	23.6	1.33	227	41.9	10.3	4.7	4.4	3.2	0.01
Rauch	84.6	3.68	0.39	11.1	1.74	312	42.4	17.3	6.6	7.1	5.4	0.02
Tres Arroyos	78.2	2.21	0.18	14.4	2.73	541	48.2	21.0	7.5	9.3	7.4	0.07
Patagones	40.0	0.99	0.08	13.9	2.42	354	39.8	14.7	4.9	7.2	7.3	0.05
Grand Mean	–	2.76	0.24	13.9	1.77	446	48.4	17.6	10.0	7.2	6.1	0.05
SD	–	1.82	0.13	3.6	0.50	171	19.5	6.0	4.8	1.8	1.7	0.03
RSD%	–	66	55	26	28	38	40	34	48	25	28	58

SD: standard deviation; RSD%: relative standard deviation.

TN contents ranged from ~0.1% in Patagones to ~0.6% in San Nicolás, average $\pm$ standard deviation of $0.24 \pm 0.13\%$ (Table 2), with a similar soil textural classes association as TOC. TOC and TN stoichiometric relationship (C:N) showed rather homogeneous values (13.9 ± 3.6 ; RSD = 26%) in the range of croplands soils (C:N = 11.8–16.0; Kirkby et al., 2011; Ghaley et al., 2015) and grasslands

soils (C:N = 11.0–16.6; Cleveland and Liptzin, 2007; Mulder and Elser, 2009; Griffiths et al., 2012; He et al., 2012; Zhao et al., 2015) indicating a predominant contribution of plant detritus from crops or natural graminaceous vegetation.

Figure 2 Soil grain size composition and TOC contents (see online version for colours)



3.2 Heavy metals

Table 2 presents heavy metal concentration in soils. Concentrations followed heavy metal natural abundances and decreased from Fe (1.01–2.73%) > Mn (194–747 $\mu\text{g g}^{-1}$) > Zn (26.8–111 $\mu\text{g g}^{-1}$) > Cu (9.5–32.6 $\mu\text{g g}^{-1}$) > Pb (3.9–19.2 $\mu\text{g g}^{-1}$) > Cr (4.3–11.9 $\mu\text{g g}^{-1}$) > Ni (2.9–9.4 $\mu\text{g g}^{-1}$) > Cd (0.01–0.11 $\mu\text{g g}^{-1}$). Most of the elements showed homogeneous spatial patterns (RSD < 50%), with higher variability for Cd (RSD = 58%). Pearson's correlation analysis revealed significant relationships between Ni and Cr, Ln Zn, Fe, Mn, Cu and Ln Pb; Mn with Cu, Ln Pb, Cd and Ln Zn; and Cr with Fe and Ln Zn (Table 3).

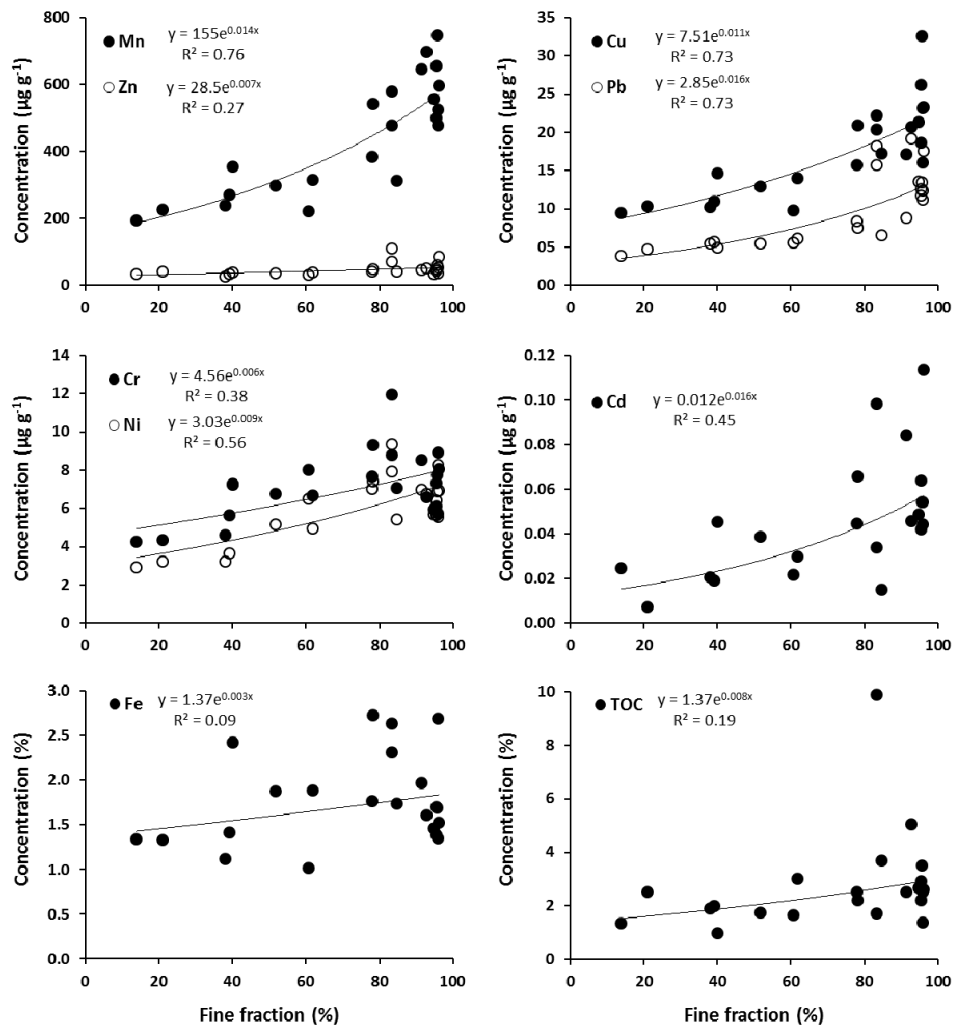
Table 3 Person's correlation coefficients among metals

	<i>Fe</i>	<i>Mn</i>	<i>Log Zn</i>	<i>Cu</i>	<i>Log Pb</i>	<i>Cr</i>	<i>Ni</i>	<i>Cd</i>
Fe	–	ns	ns	ns	ns	0.74	0.72	ns
Mn		–	0.64	0.90	0.85	ns	0.66	0.66
Log Zn			–	0.68	0.73	0.74	0.72	ns
Cu				–	0.78	ns	0.66	ns
Log Pb					–	ns	0.66	ns
Cr						–	0.92	ns
Ni							–	ns
Cd								–

ns: no significant ($\alpha = 0.002$).

Concentrations of Zn and Cr in San Nicolás soil (Ln transformed data) were atypically high (one-sided Grubbs test) suggesting some degree of pollution. In fact, San Nicolás has one of the most important steel factory complexes of Argentina, processing raw material (iron, limestone, dolomite, coke and other minerals) in blast furnaces for the production of metal tubes, plates and sheets made of steel and other iron alloys, aluminium and zinc. This industrial activity was also evidenced by the pattern of other metals such as Cu, Pb and Ni (Table 2). The other sampling sites did not show atypical concentrations despite the different land use patterns and soil type.

Figure 3 Covariation of heavy metals and TOC with fine contents in soil



Except for San Nicolás atypically increased values, Humid Pampa soil heavy metal concentrations were generally low, in the range of the lowest values of other agricultural and mean worldwide soils (Table 4). Previous studies in agricultural soils from the Buenos Aires Province established that heavy metal contents were related to parent

material and pedogenetic processes but not to recent contamination (Lavado and Porcelli, 2000; Lavado et al., 2004; Lavado, 2006).

Humid Pampa soil heavy metal contents were strongly controlled by fine grain size fractions (<0.050 mm) which presented significant ($\alpha = 0.05$) positive correlations with Mn, Cu, Pb, Ni, Cd and Cr (R^2 : 0.76, 0.73, 0.73, 0.56, 0.45, 0.38, respectively; Figure 3). These positive correlations between heavy metals and fine grain size soil fractions, enriched in clay minerals, are well established (Dudka, 1993; Kabata-Pendias and Mukherjee, 2007; Kabata-Pendias, 2011; Gupta and Bhattacharyya, 2012).

Heavy metal concentrations are below the Soil Environmental Quality Guidelines for Agriculture land use (Table 4) established in the Argentinean Legislation (1992) and even lower than the strict international soil quality guidelines of Canada (Soil Quality Guidelines for the Protection of Environmental and Human Health – Agricultural Use; CCME, 2018), China (Environmental Quality Standard for Soils; Du et al., 2015) and Netherlands (Soil Quality Reference Values; Vegter, 1995).

To evaluate anthropic vs. natural sources of heavy metals, soil enrichment factors (Figure 4), relative to crustal abundances, were calculated as the ratio of soil metal concentration to the upper continental crust content (Wedepohl, 1995). Humid Pampa (HP) soil enrichment factors, were in general low (HP_{Mn} : 0.37–1.42; HP_{Zn} : 0.52–2.13; HP_{Cu} : 0.62–2.28; HP_{Pb} : 0.23–1.13; HP_{Cr} : 0.12–0.34; HP_{Ni} : 0.16–0.50; HP_{Cd} : 0.07–1.11), in the range of enrichment factors reported for grand mean surface soils values (Kabata-Pendias and Mukherjee, 2007) reflecting a predominance of natural sources. Only for Zn, in San Nicolás site, the estimated soil enrichment factor was atypically high (enrichment value: 2.13; one-sided Grubbs test) confirming some degree of pollution in the area.

Figure 4 Heavy metal enrichment factors in relation to upper continental crust mean concentrations of Humid Pampa soil (HP, average $\pm$ standard deviation) compared to enrichment factors reported for grand mean worldwide surface soil (SEF_{crust})

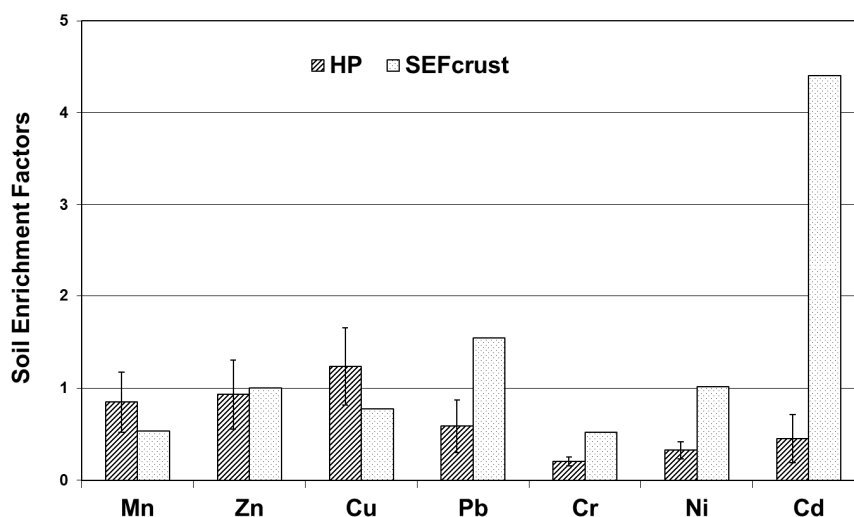


Table 4 Heavy metal concentrations in agricultural and worldwide soils

	Fe	Mn	Zn	Cu	Pb	Cr	Ni	Cd	References
	%								
	µg/g								
This study	1.01–2.73	194–747	26.8–111	9.5–32.6	3.9–19.2	4.3–11.9	2.9–9.4	0.01–0.11	
Argentina ^a (Buenos Aires Province)	2.09	449–660	16–69	3.7–23	5.0–38	6.0–25	2.0–11	0.50–1.3	Lavado and Porcelli (2000), Lavado et al. (2004) and Lavado (2006)
China ^a	–	40–1,681	20–322	8.2–515	10–184	28–111	3.1–94	0.01–1.4	Chen et al. (1997), Niu et al. (2013) and Guo et al. (2013)
Iran ^b	–	–	218	36.1	16.5	67.9	36.9	0.77	Hani and Pazira (2011)
Nigeria ^c	–	71.8	20.3	–	4.64	16.0	3.97	0.83	Ihedioha et al. (2016)
Poland ^a	0.09–2.9	37–1,380	8.0–692	<1.0–45.4	7.0–213	2.0–81.8	<2.0–48	0.08–6.5	Dudka (1992) and Loska et al. (2004)
Spain ^a	0.66–2.0	103–406	20–89	13–77	6.8–101	15–43	11–32	0.10–0.88	Micó et al. (2006)
Switzerland ^a	–	–	48–89	21–24	19–20	–	14–26	0.23–0.27	Desaules (2012)
USA ^a	2.6 ^b	<2–7,000	<5–2,900	0.45–700	2.1–700	1.0–1,000	<5–700	–	Shacklette and Boerngen (1984) and Aelion et al. (2008)
Worldwide soils ^c	3.20	761	59.8	25.8	29.2	84.0	50.0	0.35	Ure and Berrow (1982)
Worldwide soils ^d	3.50 ^e	270–525	45–100	13–24	22–44	12–83	12–34	0.37–0.78	Kabata-Pendias and Pendias (2001), and Kabata-Pendias and Mukherjee (2007)
<i>Threshold values for agriculture use</i>									
Argentina	–	–	600	150	375	750	150	3.0	Argentinean Legislation (1992)
Canada	–	–	250	63	70	64	45	1.4	CCME (2018)
China	–	–	200	50	250	150	40	0.3	Du et al. (2015)
Netherlands	–	–	140	36	85	100	35	0.8	Vegier (1995)

–: not available

^aRange of values.^bMean values.^cGrand mean.^dRange of estimated means.^eMedian value for world soils.

4 Conclusions

Associated with their main loessic origin, Humid Pampa soil textural classes were dominated by fine size fractions. C:N stoichiometric relationships indicate that plant detritus was the predominant source of the relatively high soil organic contents. Most of the heavy metals showed a significant positive correlation with fine grain size fractions. Heavy metal concentrations and estimated enrichment factors indicate that these soils, mostly dedicated to agriculture and livestock production, were not significantly affected by recent contamination, except for San Nicolás site with some degree of pollution related to the proximity to one of the most important metallurgy and steel industrial areas of Argentina.

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